Electronic Spectra of Octahedral Nickel(II) and Cobalt(II) : Complexes with 2-(2-Pyridyl)imidazole and 2-(2-Pyridyl)benzimidazole (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 58, No. 2, 1980

Electronic Spectra of Octahedral Nickel(II) and Cobalt(II) Complexes with 2-(2-Pyridyl)imidazole and 2-(2-Pyridyl)benzimidazole

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Received January 21, 1980

Absorption spectra of nickel(II) and cobalt(II) tris complexes with 2-(2-pyridyl)imidazole (PI) and 2-(2-pyridyl)benzimidazole (PBI) in solution were studied. The d-d bands were assigned according to the Tanabe-Sugano diagrams for d^7 and d^8 electronic configurations and the ligand-field parameters were estimated. PI and PBI give rise to larger crystal-field splitting and larger Racah parameter B than 2, 2′-bipyridyl and *o*-phenanthroline do.

KEY WORDS: α-Diimine/ Nickel(II) and cobalt(II) complexes/ Electronic spectra/ Ligand-field parameter/

INTRODUCTION

Metal complexes with ligands possessing α-diimine structure have been prepared and their magnetic and spectroscopic behaviors have been interpreted in terms of ligand-field theory.[1] Particularly the iron(II) complexes have interesting properties. The stable tris complexes of iron(II) with 2, 2′-bipyridyl (bipy) and *o*-phenanthroline (phen) are diamagnetic and exhibit Laporte-allowed charge-tranfer bands in the visible spectra. The tris complexes with 2-(2-pyridyl)imidazole (PI) and 2-(2-pyridyl)benzimidazole (PBI) exhibit a spin-equilibrium between $^5T_2$ and $^1A_1$ states.[2-5] Orgel suggested that the diamagnetism of $[Fe(phen)_3]^{2+}$ salts can not be expected from simple ligand-field calculations in which crystal-field splitting, Δ, is smaller than mean spin-pairing energy, π (Fe^{2+}; 17,600cm^{-1}).[6] The complex-formation must, therefore, produce a marked decrease in π from the estimated free ion value.

Analysis of d-d bands plays an important role in studying the interation between central ions and ligands in complexes. In the iron(II) complexes containing ligands with α-diimine structure, it is impossible to measure d-d band spectra because of the charge-transfer bands in the visible region. However, it becomes often possible to measure d-d band spectra when the metal ion is changed to another ion such as nickel(II) or cobalt(II). Jørgensen[8] and Robinson *et al.*[9] measured the spectra of $[Ni(bipy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ complexes. Palmer and Piper obtained the polarized crystal spectra of tris 2, 2′-bipridyl complexes of some metal ions and pointed out that the trigonal distortion in the nickel(II) complexes is very small and the Recah parameter B decreases markedly from the free-ion value.[9] The author studied the absorption spectra of nickel(II)

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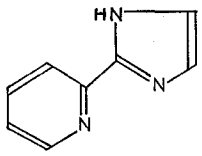
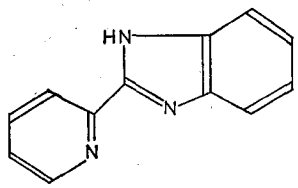


2-(2-PYRIDYL)IMIDAZOLE
(PI)



2-(2-PYRIDYL)BENZIMIDAZOLE
(PBI)

and cobalt(II) complexes with 2-(2-pyridyl)imidazole and 2-(2-pyridyl)benzimidazole in solution and will report the results here.

EXPERIMENTAL

2-(2-Pyridyl)imidazole and 2-(2-pyridyl)benzimidazole were prepared according to the procedures described previously.[4]

Tris[2-(2-pyridyl)imidazole]nickel(II) *Nitrate Dihydrate*, $[Ni(PI)_3](NO_3)_2 2H_2O$. Solutions of 2-(2-pyridyl)imidazole (1.5g) in ethanol (10ml) and nickel nitrate hexahydrate (1.0g) in water (10ml) were mixed. Ethanol was removed from the violet mixture at reduced pressure and the violet crystals were then obtained from the residual solution after a day.

Tris[2-(2-pyridyl)imidazole]cobalt(II) *Perchlorate Monohydrate*, $[Co(PI)_3](ClO_4)_2H_2O$. Solutions of 2-(2-pyridyl)imidazole (1.1g) in ethanol (10ml) and cobaltous chloride hexahydrate (0.6g) in water (10ml) were mixed and the mixture was heated for 5 hrs on a steam bath. Sodium perchlorate (0.6g) in water (10ml) was added to the cooled solution and ethanol was removed at reduecd pressure; the orange crystals were then precipitated.

Tris[2-(2-pyridyl)benzimidazole]cobalt(II) *Perchlorate Monohydrate*, $[Co(PBI)_3](ClO_4)_2H_2O$. This complex was prepared similarly from 2-(2-pyridyl)benzimidazole; yellowish-orage crystals.

Tris[2, 2′-bipyridyl]nickel(II) Chloride Heptahydrate, $[Ni(bipy)_3]Cl_2 7H_2O$, tris[*o*-phenanthroline]nickel(II) chloride heptahydrate, $[Ni(phen)_3]Cl_2 7H_2O$, and tris[2, 2′-bipyridyl]cobalt(II) chloride heptahydrate, $[Co(bipy)_3]Cl_2 7H_2O$, were prepared from

Table I. Analytical Data

Complex	C(%)		H(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
$[Ni(PI)_3](NO_3)_2 2H_2O$	43.92	44.06	3.68	3.85	23.63	23.55
$[Ni(bipy)_3]Cl_2 7H_2O$	49.50	49.75	5.12	5.29	11.38	11.61
$[Ni(phen)_3]Cl_2 7H_2O$	54.29	54.29	4.18	4.17	10.53	10.53
$[Co(PI)_3](ClO_4)_2H_2O$	39.72	40.52	3.03	3.26	17.49	17.73
$[Co(PBI)_3](ClO_4)_2H_2O$	49.74	50.12	3.37	3.39	14.23	14.64
$[Co(bipy)_3]Cl_2 7H_2O$	49.89	49.73	5.00	5.29	11.67	11.60

nickel chloride or cobaltous chloride, and 2, 2′-bipyridyl or *o*-phenanthroline. The elemental analyses for the complexes were listed in Table I.

Optical absorption measurements were made on a Hitachi 323 automatic recording spectrophotometer and ethanol was used as solvent. $[Ni(PBI)_3]^{2+}$ salt could not be isolated. The absorption spectrum of $NiCl_2$ in ethanol, however, changed by the addition of 2-(2-pyridyl) benzidazole because of the complex-formation. When the concentration-ratio of 2-(2-pyridyl) benzimidazole to $NiCl_2$ was larger than 3, the spectrum did not change. Thus the author concluded that the unchanged spectrum is due to $[Ni(PBI)_3]^{2+}$.

RESULTS AND DISCUSSION

The absorption spectra of nickel(II) complexes are shown in Fig. 1. As previously reported, the first bands of the spectra of $[Ni(bipy)_3]Cl_27H_2O$ and $[Ni(phen)_3]Cl_27H_2O$ split into two components with approximately same intensity, where the magnitude of the splits is about 1, 000cm^{-1}. Though the first bands for $[Ni(PI)_3](NO_3)_22H_2O$ and $[Ni(PBI)_3]^{2+}$ split as well, the relative intensity-ratio of the two components is far from 1 and the magnitude of the splits is about 1, 500cm^{-1}.

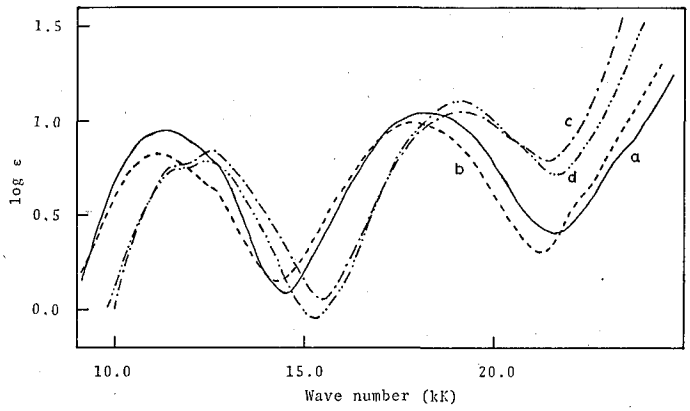


Fig. 1. Absorption spectra of nickel(II) complexes.
a: $[Ni(PI)_3](NO_3)_22H_2O$, b: $[Ni(PBI)_3]^{2+}$, c: $[Ni(bipy)_3]Cl_27H_2O$,
d: $[Ni(phen)_3]Cl_27H_2O$

It is well-known that some octahedral nickel(II) complexes exhibit splitting absorption bands. The explanation for the splitting are probably ascribed to (i) split of the $^3T_2$ and the $^3T_1$ states due to the spin-orbit coupling, or (ii) split of these states due to some ligand-field with low symmetry. The polarized crystal spectra of $[Zn(Ni)(bipy)_3]SO_47H_2O$ shows that the trigonal distortion is very small.[9] Ballhausen and Liehr assigned the double band of $[Ni(H_2O)_6]^{2+}$ to the spin-orbit components of the $^3T_1$ level.[10,11] Jørgensen and Robinson *et al.* investigated absorption spectra of many nickel(II) complexes and assigned the double bands of $[Ni(phen)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$ salts to the spin-allowed $^3A_2 \rightarrow {}^3T_2$ and to the spin-forbidden $^3A_2 \rightarrow {}^1E$ transitions.[7,8] This problem does not come to a conclusion at present. Taking account of the spin-orbit coupling by

means of the first-order perturbation, the $^3T_2$ state splits into A_2, T_2, E and T_1 states and the magnitude of the split of the $^3T_2$ state is equal to $3\lambda(^3T_2)$, where $\lambda(^3T_2)=-\xi/4$, and $\xi=630cm^{-1}$ in free Ni^{2+} ion. Therefore, we can expect that the magnitude of the split has to become about $480cm^{-1}$. But this result is not consistent with the experimental data in this study. If we were to take account of the spin-orbit coupling by means of the secondary perturbation, the disagreement would not be improved. When crystal-field splitting, Δ, is considerably large, the ^1E state lies close to the $^3T_2$ level and the spin-forbidden transition $^3A_2\rightarrow{}^1E$ is allowed through the spin-orbit interaction, $\mathcal{H}_{so}$. Taking account of the interaction by means of the first-order pertubation, the wave function of the ^1E state is written by the following equation:

$$\Psi'(^1E)=\Psi(^1E)+\frac{\langle\Psi(^3T_2)\,|\,\mathcal{H}_{so}\,|\,\Psi(^1E)\rangle}{E(^1E)-E(^3T_2)}\Psi(^3T_2) \qquad (1)$$

where $\Psi(^1E)$ and $\Psi(^3T_2)$ are wave functions for the ^1E and the $^3T_2$ states, respectively and $E(^1E)-E(^3T_2)\,(=\Delta E)$ is the separation between these states. Thus the oscillator strength of the spin-forbidden transition is given by:

$$f\simeq f_{allowed}\left(\frac{\langle\mathcal{H}_{so}\rangle}{\Delta E}\right)^2 \qquad (2)$$

where $\langle\mathcal{H}_{so}\rangle=\langle\Psi(^3T_2)\,|\,\mathcal{H}_{so}\,|\,\Psi(_1E)\rangle$ and $f_{allowed}$ is the oscillator strength of the spin-allowed transition $^3A_2\rightarrow{}^3T_2$. Equation (2) means that a large ΔE value gives rise to the spin-forbidden transition with low intensity. Therefore, it is qualitatively consistent with the theory to assign the double bands observed in this study to the transitions $^3A_2\rightarrow{}^3T_2$ and $^3A_2\rightarrow{}^1E$, as previously proposed.[7,8] On the other hand, the magnitude of the split of the $^3T_1$ state due to the spin-orbit effect is estimtated to be about $1,300cm^{-1}$ for free Ni^{2+} ion, which is consistent with the experimental data of $[Ni(H_2O)_6]^{2+}$ $(1,400cm^{-1})$. But the Δ value of this ion is small $(\Delta=8,500cm^{-1})$. Therefore, the ^1E state lies probably close to the $^3T_1$ level and it is also expected that the oscillator strength of the spin-forbidden transition $^3A_2\rightarrow{}^1E$ is considerably large. Thus it is difficult to assign the double band of $[Ni(H_2O)_6]^{2+}$.

Fig 2 shows the absorption spectra of the cobalt(II) complexes. $[Co(PBI)_3](ClO_4)_2$-H_2O was insoluble in the solvent. The absorption maxima and the assignment are listed

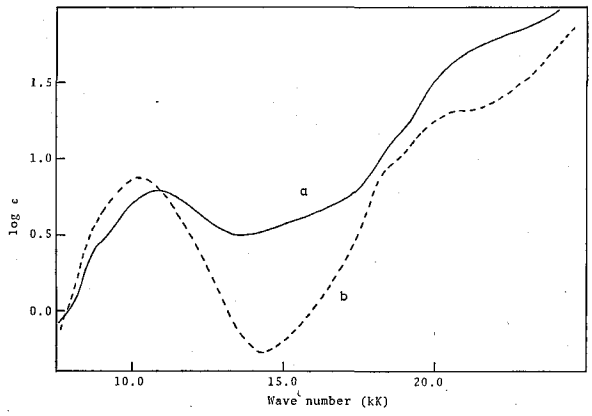


Fig. 2. Absorption spectra of cobalt(II) complexes.
a: $[Co(bipy)_3]Cl_2 7H_2O$, b: $[Co(PI)_3](ClO_4)_2H_2O$

Table II. d-d Band Maxima of Nickel(II) Complexes

Complex	d-d Band	(log ε)	Excited Sate
$[N(bipy)_3]Cl_27H_2O$	11,490[a]	(0.76)	^1E
	12,560	(0.84)	$^3T_2$
	19,050	(1.04)	$^3T_1$
	20,830[a]	(0.85)	$^1A_1$
$[Ni(phen)_3]Cl_27H_2O$	11,570[a]	(0.73)	^1E
	12,550	(0.78)	$^3T_2$
	19,080	(1.10)	$^3T_1$
	20,880[a]	(0.84)	$^1A_1$
$[Ni(PI)_3](NO_3)_22H_2O$	11,210	(0.94)	$^3T_2$
	12,740[a]	(0.76)	^1E
	18,280	(1.04)	$^3T_1$
	23,260[a]	(0.79)	$^1A_1$
$[Ni(PBI)_3]^{2+}$	11,140	(0.82)	$^3T_2$
	12,710[a]	(0.63)	^1E
	17,920	(0.99)	$^3T_1$
	22,470[a]	(0.60)	$^1A_1$

unit: cm^{-1}, a: shoulder

Table III. d-d Band Maxima of Cobalt(II) Complexes

Complex	d-d Band	(log ε)	Excitd State
$[Co(bipy)_3Cl_2]7H_2O$	8,810[a]	(0.42)	^2E
	10,800	(0.79)	$^4T_2$
	18,520[a]	(1.10)	$^2T_1(P)$
	21,280	(1.73)	$^4T_1$
$[Co(PI)_3](ClO_4)_2H_2O$	10,160	(0.86)	$^4T_2$
	18,520[a]	(0.96)	$^2T_1(P)$
	20,830	(1.32)	$^4T_1$

unit: cm^{-1}, a: shoulder

in Tables II and III. The bands are assigned according to the Tanabe-Sugano diagrams for octahedral d^7 and d^8 complexes.[12] The cobalt complexes are high-spin ($^4T_1$ ground state). Assuming that the bands at 10,800 and 21,280cm^{-1} in the spectrum of $[Co(bipy)_3]Cl_27H_2O$ are due to the $^4T_1 \rightarrow {}^4T_2$ and $^4T_1 \rightarrow {}^4T_1(P)$ transitions, respectively, we can obtain that $\Delta = 11,120 cm^{-1}$ and $B = 794 cm^{-1}$ (B; Racah parameter). From the values of Δ and B, the energies of the other transitions are calculated to be 6,500cm^{-1} ($^4T_1 \rightarrow {}^2E$), 15,330cm^{-1} ($^4T_1 \rightarrow {}^2T_2$ or $^2T_1$), 18,520cm^{-1} ($^4T_1 \rightarrow {}^2T_1(P)$) and 21,280$cm^{-1}$ ($^4T_1 \rightarrow {}^4A_2$). The transition $^4T_1 \rightarrow {}^4A_2$ is a double excitation and its intensity might be very low. The transitions $^4T_1 \rightarrow {}^2T_2$ or $^2T_1$ are found at 16,000cm^{-1} in the single crystal spectrum of $[Zn(Co)(bipy)_3]SO_47H_2O$.[9] Therefore, the flat of the spectrum in this study at 15,500cm^{-1} might be due to the transitions. The band at 18,520cm^{-1} might be due to the transition $^4T_1 \rightarrow {}^2T_1(P)$ as well. The ligand-field parameters obtained from the assignments are listed in Table IV. The parameters of $[Ni(bipy)_3]Cl_27H_2O$ and $[Co(bipy)_3]Cl_27H_2O$ are consistent with the values reported previously.[9] 2-(2-Pyridyl)imidazole and 2-(2-pyridyl)benzimi-

Table IV. Ligand-field Parameters

Complex	$\Delta(cm^{-1})$	$B(cm^{-1})$	β
$[Ni(bipy)_3]Cl_2 7H_2O$	12,560	672	0.65
$[Ni(phen)_3]Cl_2 7H_2O$	12,550	671	0.65
$[Ni(PI)_3](NO_3)_2 2H_2O$	11,210	747	0.73
$[Ni(PBI)_3]^{2+}$	11,140	743	0.72
$[Co(bipy)_3]Cl_2 7H_2O$	11,120	794	0.82
$[Co(PI)_3](ClO_4)_2 H_2O$	10,640	825	0.85

Δ: crystal-field splitting, B: Racah parameter,
$\beta = B_{complex}/B_{free\ ion}$: nephelauxetic ratio

dazole give rise to larger Δ and B value than 2, 2′-bipyridyl and *o*-phenanthroline do. The B values of the complexes used in this study decrease markedly from the values for the free ions. Particularly the values of the nickel(II) complexes represent about 30% lowering from the free-ion value ($1,030 cm^{-1}$). In this connection, the B value of $[Ni(H_2O)_6]^{2+}$ is $945 cm^{-1}$, which represents about 10% lowering.

ACKNOWLEDGMENT

The author wishes to thank Professor T. Shigematsu for his encouragement in this study.

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